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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

MAR 3 1989

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

## MEMORANDUM

SUBJECT: PP#9E3704: 2,4-D (Geographical Restriction, MN Only) in Raspberries, EPA Reg. No. 50534-13. Evaluation of Residue Data and Analytical Methodology.  
(MRID# 408814-00, and 01 DEB# 4684).

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THRU: Philip V. Errico, Section Head *Philip V. Errico*  
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and  
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BACKGROUND

The IR-4 National Director, Dr. R. H. Kupelian, the IR-4 project No. 4, State Agricultural Experiment Stations of Rutgers University, New Brunswick, New Jersey 08903, on behalf of the IR-4 project and the Agricultural Experiment Station of Minnesota request the establishment of a tolerance for the residue of 2,4-dichlorophenoxyacetic acid (2,4-D) in or on the raw agricultural commodity raspberries at 0.1 ppm. This tolerance is with the geographical restriction : For use in the state of Minnesota only.

Tolerances are established for residues of the herbicide, plant regulator and fungicide 2,4-D in or on numerous raw agricultural commodities ranging from 0.1 ppm in blueberries, to 1000 ppm in grasses, pasture, and rangeland [CFR 40 180.142 (a,

b, c, d, e, f, and h)]. The Guidance for the Reregistration of Pesticide Products Containing 2,4-D as the Active Ingredient was published on September 1988.

### Conclusions:

1a. According to the recently completed residue chemistry chapter of the 2,4-D Registration Standard, the nature of the residue in plants is not adequately understood. However because this is a minor crop, the spray is directed away from the plant parts, and there are no detectable residues even at the 2x rate ( $<0.05$  ppm), we will recommend regulating only the parent compound. If the requested plant metabolism studies identify new metabolites requiring regulation, additional field trial data may be necessary to support the established tolerance.

1b. There are no animal feed items involved in this petition; therefore, there are no expectations of secondary residues in meat, milk, poultry, and eggs from this proposed use.

2. There is a GC analytical method for enforcement purposes for 2,4-D and its metabolite dichlorophenol (DCP). This method has been submitted to FDA for publication in PAM II( memo of F. D. Griffith, Jr, PP# 4E3060, 2/16/88).

3. With a geographically restricted registration to the state of MN only, the proposed tolerance for the residues of 2,4-D on raspberries at 0.1 ppm is supported by the residue data.

4. An International Residue Limit Status sheet is attached. There are no Mexican limit for 2,4-D on raspberries. There are Codex limits for 2,4-D at 0.1 ppm on red and black raspberries. There is also a Canadian limit for 2,4-D at 0.1 ppm on raspberries. The establishment of the recommended tolerance for 2,4-D at 0.1 on raspberries is in harmony with the International Residue Limits.

### Recommendation

Tox considerations permitting and with the proposed use restricted to the state of Minnesota only, we can recommend for the proposed tolerance of 0.1 ppm for residues of 2,4-dichloro-phenoxyacetic acid (2,4-D) in or on raspberries.

### Detailed Considerations

### Manufacturing and Formulation

2,4-D (DACAMINE 4D) is an oil-soluble diamine form of 2,4-D which is formulated to be used only with water. It contains 31.7% N-oley-1,3-propylenediamine salt of 2,4-dichlorophenoxyacetic

acid, 21.6% 2,4-Dichlorophenoxyacetic acid, and 46.7% inert ingredients. This is equal to 3.6 lb of acid equivalent per gallon. Review of inerts for clearance under 40 CFR 180.1001 is now within the purview of the Registration Division. The 2,4-D registration standard has requested information in the manufacturing process for the technical product. This data requirement will be handled in the re-registration process for this proposed minor use.

#### Proposed Use

2,4-D will control weeds, when applied as a spray directed away from raspberry plants with ground equipment, at a rate up to 3 pints ( 1.4 lbs ai) per acre, in sufficient water to cover the weeds surface thoroughly. The spray should not drift to contact any parts of the raspberry plants. First application is made before or after harvest when weeds are vigorously growing. A second spray may be applied if necessary. Do not apply within 24 days of harvest. The use of this product on raspberries is restricted to the state of Minnesota.

#### Nature of the Residue

##### Plant Metabolism

No plant metabolism study was submitted with this petition.

According to the Residue Chemistry Chapter of the 2,4-D Registration Standard (FRSTR 1/29/1988), and the Guidance for the reregistration of 2,4-D( September 1988), plant metabolism is not adequately understood. The following additional data are required.

° Data depicting the total terminal residue of ring-labeled [ $^{14}\text{C}$ ]2,4-D in three representative, dissimilar crops (potatoes, a grain crop, and an orchard fruit crop) are required. Residues must be characterized in the raw agricultural commodities produced following application of formulated [ $^{14}\text{C}$ ]2,4-D to the crops under conditions representing normal cropping practices. Exaggerated dosages may be necessary in order to have sufficient  $^{14}\text{C}$ -residues present for characterization.  $^{14}\text{C}$ -Residues must also be analyzed by analytical methods suitable for tolerance enforcement.

However because this is a minor crop, the spray is directed away from the plant parts, and there are no detectable residues even at the 2x rate (<0.05 ppm), we will recommend regulating only the parent compound. If the requested plant metabolism studies identify new metabolites requiring regulation, additional field

trial data may be necessary to support the established tolerance.

### Animal Metabolism

No animal feed items are involved in this petition, therefore there is no concern for secondary residues in meat, milk, poultry and eggs from this proposed use.

### Analytical Method

There is a GC analytical method available for enforcement purposes which determines 2,4-dichlorophenoxy-2- butoxyethanol ester (2,4-D) and 2,4-dichlorophenol on soybeans and soybean hay. A method validation has been carried out ( PP#4E3060, 10/11/1985, memo of W. R. Bontoyan, Head of the Analytical Chemistry section,). This method converts 2,4-D (two hour acid hydrolysis) esters to the free 2,4-D acid. The 2,4-D (acid form) is methylated by diazomethane and determined by GLC. The DCP is separated from the 2,4-D acid in sample by column chromatography on 4% deactivated alumina Grade II. The 2,4-D is eluted with a 0.25 M sodium bicarbonate solution, then DCP is eluted with diethyl ether. Both compounds are measured by GLC. The GLC method uses a Hall electrolytic conductive detector with a limit of detectability of 0.05 ppm of 2,4-D acid equivalent and 0.05 ppm DCP, on soybeans. This method has been forwarded to FDA for publication in PAM II (memo of Frances D Griffith, Jr., PP# 4E3060, 1/3/86 and 2/16/88).

The analytical methods used in this petition are modifications to the methods of Yip (1971, J. Assoc. Offic. Anal. Chem. 54: 966-969) and Kan, et al, (1981, J. Assoc. Offic. Anal. Chem. 64:1305-8). The method is summarized below.

### Summary:

2,4-dichlorophenoxyacetic acid (2,4-D) is analyzed by an adaptation of the method described by Yip (1971). The phenoxy acid is extracted from the tissue with acetonitrile-water. The acetonitrile layer is removed and the aqueous layer is acidified and extracted and determined with methylene chloride. After concentration of the methylene chloride solvent, the methyl ester of the 2,4-D is gas chromatographed with a Hall Electrolytic Conductivity Detector.

The extraction and analysis of 2,4-dichlorophenol(DCP) is based on a method by Kan, et al, (1981). The tissue is placed in an acidic aqueous solution and DCP is steam distilled from the mixture. The DCP is trapped in a toluene solution, which is analyzed directly by gas chromatography, with a Hall electrolytic conductivity detector.

The results indicates that, samples fortified with the parent compound at 0.05 ppm and 0.25 ppm gave recoveries of 90% to 102 % for 2,4-D, and 91% to 110% for DCP. 2,4-D and DCP are stable in raspberries samples fortified with parent compound when stored at -20 °C for at least four months.

Residue Data:

Field residue trials were conducted in Minnesota at one application rate of 1.4 (1X) or 2.8 (2X) lbs. of ai/acre, on raspberries. The 2,4-D formulation was applied to the raspberry fields 24 days before harvest (pre-harvest). The plot size was 10 X 30 feet with 4 replications.

Mature treated and untreated raspberries samples were frozen at -8 °F at harvest and were stored for three weeks before shipping frozen to the analytical laboratories at North Dakota State University. Samples were kept frozen at -20 °C and were analyzed in less than 4 months after harvest.

The field samples did not contain detectable amounts (<0.05 ppm) of 2,4-D or DCP, at either the 1X (1.4 lbs. ai/A ) or 2X rates. Controls were reported as <0.05 ppm for both 2,4-D and DCP.

The submitted residue data supports the requested tolerance of 0.1 ppm in or on raspberries for this proposed use geographically restricted to Minnesota.

Meat, Milk, Poultry and Egg

There are no feed items involved in this petition, therefore no secondary residues are expected in meat, milk, poultry or eggs from this proposed use on raspberries.

cc: PP#9E3704, 2,4-D, Acting Chief R.D.Schmitt, RF., SF., R.B. Jaeger (SAOS/HED), Reviewer (F. Toghrol), Circ., PMSD/ISB (Eldrige).

TDI: Section Head P.V.Errico: 2/28/89, R. Loranger: 2/28/89  
H7509C DEB: Reviewer F.T.: RM:802, CM#2: 557-7887, 2/28/89.